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<p>(54) Title: PHOTOTHERMOGRAPHIC RECORDING MATERIAL COATED FROM AN AQUEOUS MEDIUM</p>		
<p>(57) Abstract</p> <p>A photothermographic recording material comprising a support and a photo-addressable thermally developable element comprising photosensitive silver halide in catalytic association with a substantially light-insensitive silver salt of an organic carboxylic acid, an organic reducing agent for the substantially light-insensitive silver salt of an aliphatic carboxylic acid in thermal working relationship therewith and a binder, characterized in that the binder comprises a non-proteinaceous water-soluble binder, a non-proteinaceous water-dispersible binder (preferably comprising a diene, styrene, an acrylate or a methacrylate monomer) or a mixture of a non-proteinaceous water-soluble binder and a non-proteinaceous water-dispersible binder and the photo-addressable thermally developable element is capable of being coated from an aqueous medium and is capable of producing images stable to light without a wet-processing step; a process for producing the photothermographic recording material and a photothermographic recording process therefor.</p> 		

Photothermographic recording material coated from an aqueous medium.

#### Field of the invention

The present invention relates to a photothermographic recording material comprising a photo-addressable thermally developable element coatable from aqueous media.

#### Background of the invention.

Thermal imaging or thermography is a recording process wherein images are generated by the use of thermal energy.

In thermography three approaches are known:

1. Direct thermal formation of a visible image pattern by imagewise heating of a recording material containing matter that by chemical or physical process changes colour or optical density.

2. Imagewise transfer of an ingredient necessary for the chemical or physical process bringing about changes in colour or optical density to a receptor element containing other of the ingredients necessary for the chemical or physical process followed by uniform heating to bring about the changes in colour or optical density.

3. Thermal dye transfer printing wherein a visible image pattern is formed by transfer of a coloured species from an imagewise heated donor element onto a receptor element.

Thermographic materials of type 1 can be rendered photothermographic by incorporating a photosensitive agent which after exposure to UV, visible or IR light is capable of catalyzing or participating in a thermographic process bringing about changes in colour or optical density.

Examples of photothermographic materials are the so called "Dry Silver" photographic materials of the 3M Company, which are reviewed by D.A. Morgan in "Handbook of Imaging Science", edited by A.R. Diamond, page 43, published by Marcel Dekker in 1991.

US-P 3,152,904 discloses an image reproduction sheet which comprises a radiation-sensitive heavy metal salt which can be reduced to free metal by a radiation wave length between an X-ray wave length and a five microns wave length and being distributed substantially uniformly laterally over the sheet, and as the image forming component an oxidation-reduction reaction combination which is substantially latent under ambient conditions and which can be

hexadecylsulfinate, silver dodecylsulfinate, silver nonylsulfinate, silver 3-phenylpropylsulfinate, and silver cyclohexylsulfinate, and wherein the binder is a latex. In a preferred embodiment, according to US-P 4,529,689, (a) is silver hexadecylsulfinate, (b) is a chemically sensitized gelatino-silver halide negative or direct positive emulsion, (c) is a phenidone or dimezone moiety, and (d) is an acrylate latex. According to the detailed description of US-P 4,529,689 representative examples of the latex polymer or copolymer are butylmethacrylate, methylmethacrylate, ethylmethacrylate, polystyrene, methylmethacrylate-acrylic acid etc. Furthermore, in all the examples according to the invention disclosed in US-P 4,529,689, it is necessary after exposure and thermal development of the photothermographic film composition to fix it for 1 minute with ammonium thiosulfate followed by washing in running water and drying to avoid print up (darkening) of the unexposed areas of the image. This necessity for the wet fixing of the photothermographic film compositions disclosed in the invention examples of US-P 4,529,689 removes the essential advantage of so-called "Dry Silver" photothermographic materials over classical silver halide emulsion materials namely the avoidance of wet processing.

Thus, despite forty years of continuous research in this area, a production method for photothermographic materials based on a substantially light-insensitive organic silver salt, photosensitive silver halide in intimate catalytic association with the organic silver salt and a reducing agent for the organic silver salt which dispenses with these disadvantages of the current teaching, has to our knowledge not yet been developed.

Objects of the invention.

It is a first object of the invention to provide a photothermographic recording material comprising a photo-addressable thermally developable element with excellent image-forming properties.

It is a second object of the invention to provide a photothermographic recording material comprising a photo-addressable thermally developable element based on a substantially light-insensitive organic silver salt, photosensitive silver halide in catalytic association therewith and an organic reducing agent for the organic silver salt, which is produceable without necessitating intermediate drying of the organic silver salt acid.

support.

A photothermographic recording process is further provided comprising the steps of: (i) image-wise exposing a photothermographic recording material, as referred to above, to a source of actinic radiation to which the photothermographic recording material is sensitive; and (ii) thermally developing the image-wise exposed photothermographic recording material.

Preferred embodiments of the present invention are disclosed in the detailed description of the invention.

Detailed description of the invention.

The invention is described hereinafter by way of examples with reference to the accompanying figure wherein:

FIGURE 1: shows a transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver bromide dispersion produced in the course of the preparation of invention example 69.

#### Aqueous

The term aqueous for the purposes of the present invention includes mixtures of water with water-miscible organic solvents such as alcohols e.g. methanol, ethanol, 2-propanol, butanol, iso-amyl alcohol, octanol, cetyl alcohol etc; glycols e.g. ethylene glycol; glycerine; N-methyl pyrrolidone; methoxypropanol; and ketones e.g. 2-propanone and 2-butanone etc.

#### Water-dispersible and water-soluble binders

According to the present invention the photo-addressable thermally developable element comprises a binder comprising a non-proteinaceous water-soluble binder, a non-proteinaceous water-dispersible binder or a mixture of a non-proteinaceous water soluble binder and a non-proteinaceous water-dispersible binder.

In a preferred embodiment of the present invention the binder is a polymer latex. In a particularly preferred embodiment of the present invention the polymer latex is selected from the group consisting of: an aqueous dispersion of a terpolymer consisting of 47.5% by weight of methylmethacrylate, 47.5% by weight of butadiene

Monsanto USA and provides a good adhesion to paper and properly subbed polyester supports. It should be noted that there is no clear cut transition between a polymer dispersion and a polymer solution in the case of very small polymer particles resulting in the smallest particles of the polymer being dissolved and those slightly larger being in dispersion.

Examples of suitable water-dispersed polymers, according to the present invention, are: diene-(meth)acrylate-copolymers (BINDER 01 to BINDER 04), styrene-butadiene-copolymers (BINDER 05 to BINDER 10), styrene-(meth)acrylate-copolymers (BINDER 11 to BINDER 16), acrylonitrile-copolymers (BINDER 17 to BINDER 20), (meth)acrylate-copolymers (BINDER 21 to 30), ethene-polymers and copolymers (BINDER 31), chlorinated polymers and polymers of chlorine-containing monomers (BINDER 32 to BINDER 35), polymers and copolymers of vinyl acetate (BINDER 36 to BINDER 40), various polycondensation polymers (BINDER 41 to BINDER 55), epoxy-resins (BINDER 56) and melamine resins (BINDER 57). In the case of commercial products only the main comonomers are given below with their concentrations if known. The binders of these products may contain in addition to the comonomers given below small amounts of copolymerized hydrophilic monomers, such as (meth)acrylic acid, (meth)acrylamide, maleic acid and substituted maleic acid etc. In addition tensides and plasticizers may be present and the dispersing medium may contain small quantities of water-miscible organic solvent in addition to water.

- BINDER 01: copolymer consisting of 45% by weight of methylmethacrylate, 45% by weight of butadiene and 10% by weight of itaconic acid;
- BINDER 02: terpolymer consisting of 47.5% by weight of methylmethacrylate, 47.5% by weight of butadiene and 5% by weight of itaconic acid;
- BINDER 03: copolymer consisting of 47.5% by weight of methylmethacrylate, 47.5% by weight of isoprene and 5% by weight of itaconic acid;
- BINDER 04: copolymer consisting of 50% by weight of methylmethacrylate and 50% by weight of butadiene;
- BINDER 05: BAYSTAL™ P2005 from BAYER, a copolymer on the basis of styrene and butadiene;
- BINDER 06: BAYSTAL™ P2000 from BAYER, a copolymer on the basis of styrene and butadiene;

- BINDER 26: VINNAPAS™ DISPERSION LL990 from WACKER, a (meth)acrylic acid-(meth)acrylate-copolymer;
- BINDER 27: BAYHYDROL™ VP LS 2940E from BAYER, an acrylate-polymer containing hydroxy-groups;
- BINDER 28: terpolymer consisting of 53% by weight of butylacrylate, 45% by weight of methylmethacrylate and 2% by weight of the sodium salt of 2-acrylamido-2-methyl-1-propane-sulfonic acid;
- BINDER 29: ROHAFLOC™ F50 from ROHM & HAAS, an acrylate resin;
- BINDER 30: terpolymer consisting of 85% by weight of butyl-methacrylate, 10% by weight of butylacrylate and 5% by weight of N-diaceton acrylamide;
- BINDER 31: HORDAMER™ PE02 from HOECHST, a polyethene dispersion;
- BINDER 32: HALOFLEX™ 208 from ICI, a chlorinated polyethene latex;
- BINDER 33: VINNAPAS™ E DISPERSION CEF19 from WACKER, a vinyl acetate-ethene-vinylchloride-copolymer;
- BINDER 34: IXAN™ WA36 from SOLVAY, a vinylidene chloride-containing copolymer;
- BINDER 35: IXAN™ WA50 from SOLVAY, a vinylidene chloride-methyl methacrylate-copolymer;
- BINDER 36: MOWILITH™ DO25 from HOECHST, polyvinyl acetate with 10.8% dibutyl phthalate as plasticizer and polyvinyl alcohol as emulsifier/stabilizer for the latex;
- BINDER 37: MOWILITH™ D50 from HOECHST, polyvinyl acetate with polyvinyl alcohol as emulsifier/stabilizer for the latex;
- BINDER 38: MOWILITH™ DHL from HOECHST, polyvinyl acetate with polyvinyl alcohol as emulsifier/stabilizer for the latex;
- BINDER 39: S-LEC™ KW1 from SEKISUI, a vinyl acetate, vinyl alcohol-vinyl acetal-copolymer;
- BINDER 40: BUTVAR™ DISPERSION RS3120 from MONSANTO, a vinyl butyral-vinyl alcohol-vinyl acetate-copolymer;
- BINDER 41: polyester consisting of 26.5 mole% of terephthalic acid, 20 mole% of isophthalic acid, 7 mole% of the sodium salt of sulfo-isophthalic acid and 50 mole% ethene glycol dispersed in water without tensides;
- BINDER 42: GEROL™ PS20 from RHONE-POULENC, a terephthalic acid-isophthalic acid-sulfo-isophthalic acid-ethene glycol-diethene glycol-copolyester;
- BINDER 43: EASTMAN™ AQ29D from EASTMAN-KODAK, an isophthalic acid-

- vinyl acetate;
- BINDER 61: POLYOX™ WSR N10 from UNION CARBIDE, a polyethene oxide;
- BINDER 62: gum arabic;
- BINDER 63: KLUCEL™ E from HERCULES, cellulose 2-hydroxypropyl-ether;
- BINDER 64: CELLULOSE GUM™ 12M8 from HERCULES, sodium salt of cellulose carboxymethylether.

To improve the layer-forming properties of water-soluble and water-dispersible polymers, plasticizers can be incorporated into the polymers, water-miscible solvents can be added to the dispersion medium and mixtures of water-soluble polymers, mixtures of water-dispersible polymers, or mixtures of water-soluble and water-dispersible polymers may be used.

The non-proteinaceous water-soluble and non-proteinaceous water dispersible binders of the present invention can be used together with proteinaceous binders in the photo-addressable thermally developable element. Suitable proteinaceous binders are: gelatin, modified gelatins such as phthaloyl gelatin, zein etc.

#### Photo-addressable thermally developable element

The photo-addressable thermally developable element, according to the present invention, comprises a substantially light-insensitive silver salt of an organic carboxylic acid, photosensitive silver halide in catalytic association therewith and an organic reducing agent in thermal working relationship with the substantially light-insensitive silver salt of an organic carboxylic acid and a water soluble or water-dispersible binder. The element may comprise a layer system with the silver halide in catalytic association with the substantially light-insensitive silver salt of an organic carboxylic acid, spectral sensitizer optionally together with a supersensitizer in intimate sensitizing association with the silver halide particles and the other ingredients active in the thermal development process or pre- or post-development stabilization of the element being in the same layer or in other layers with the proviso that the organic reducing agent and the toning agent, if present, are in thermal working relationship with the substantially light-insensitive silver salt of an organic carboxylic acid i.e. during the thermal development process the reducing agent and the toning agent, if present, are able to diffuse

salt to an aqueous liquid and the metered addition of the aqueous solution or suspension of the organic carboxylic acid or its salt; and/or the aqueous solution of the silver salt is regulated by the concentration of silver ions or the concentration of anions of the silver salt in said aqueous liquid.

This metered addition may be regulated by varying the rate of addition of the solution or suspension of the organic carboxylic acid or its salt; and/or the rate of addition of the solution of the silver salt so as to maintain the value of a physical parameter, that significantly changes upon the addition of the solution or suspension of the organic carboxylic acid or its salt and/or the solution of the silver salt to the liquid, at a particular value predetermined for a particular moment in the process. The value of the physical parameter used to regulate the addition of the solution or suspension of an organic carboxylic acid or its salt and/or the solution of the silver salt to the liquid may vary during the course of the production process.

Furthermore, the physical parameter used to regulate the metered addition of the solution or suspension of the organic carboxylic acid or its salt; and/or the solution of the silver salt, according to the present invention, may be the concentration of silver ions or the concentration of anions of the silver salt in the liquid. Other physical parameters that may be used to regulate the metered addition of the solutions are, for example, the electrical conductivity of the suspending medium, the dielectric constant of the suspending medium, the density of the suspending medium, the pH of the suspending medium etc.

The temperatures of the solution or suspension of the organic carboxylic acid or its salt; the solution of the silver salt; and the liquid are determined by the required characteristics of the particles; and may be kept constant or may be varied during the synthesis of the silver salt of a organic carboxylic acid again depending upon the required characteristics of the particles.

The liquid for suspending the particles may contain a non-ionic or anionic surfactant for the particles. Dispersion agents may also be present in the solution or suspension of the organic carboxylic acid or its salt; and in the solution of the silver salt; may be added via an additional jet during the production process of the suspension of particles containing a substantially light-insensitive silver salt of a organic carboxylic acid; and may be added at the end of the production process.



the range of 0.5 to 20 mol percent being preferred and the range of 1 to 12 mol percent being particularly preferred.

The silver halide may be any photosensitive silver halide such as silver bromide, silver iodide, silver chloride, silver bromoiodide, silver chlorobromoiodide, silver chlorobromide etc. The silver halide may be in any form which is photosensitive including, but not limited to, cubic, orthorhombic, tabular, tetrahedral, octagonal etc. and may have epitaxial growth of crystals thereon.

The silver halide used in the present invention may be employed without modification. However, it may be chemically sensitized with a chemical sensitizing agent such as a compound containing sulphur, selenium, tellurium etc., or a compound containing gold, platinum, palladium, iron, ruthenium, rhodium or iridium etc., a reducing agent such as a tin halide etc., or a combination thereof. The details of these procedures are described in T.H. James, "The Theory of the Photographic Process", Fourth Edition, Macmillan Publishing Co. Inc., New York (1977), Chapter 5, pages 149 to 169.

Emulsion of silver salt of an organic carboxylic  
acid and photosensitive silver halide

The silver halide may be added to the photo-addressable thermally developable element in any fashion which places it in catalytic proximity to the substantially light-insensitive silver salt of an organic carboxylic acid. Silver halide and the substantially light-insensitive silver salt of an organic carboxylic acid which are separately formed, i.e. ex-situ or "preformed", in a binder can be mixed prior to use to prepare a coating solution, but it is also effective to blend both of them for a long period of time. Furthermore, it is effective to use a process which comprises adding a halogen-containing compound to the silver salt of an organic carboxylic acid to partially convert the substantially light-insensitive silver salt of an organic carboxylic acid to silver halide as disclosed in US-P 3,457,075.

According to a preferred embodiment according to the present invention, particles of the photosensitive silver halide in the photo-addressable thermally developable element are uniformly distributed over and between particles of the substantially light-insensitive silver salt of an organic carboxylic acid, at least 80% by number of the photosensitive silver halide particles having a diameter, determined by transmission electron microscopy, of  $\leq 40\text{nm}$ .

salts, according to the present invention, may be added as solids or solutions or may be formed in the aqueous dispersion of particles of the substantially light-insensitive silver salt by metathesis between a salt with halide or polyhalide anions and onium salts with anions other than halide or polyhalide.

Preferred oniums according to the present invention are organo-phosphonium, organo-sulphonium and organo-nitrogen onium cations, with heterocyclic nitrogen onium (e.g. pyridinium), quaternary phosphonium and ternary sulphonium cations being preferred. Preferred halide anions, according to the present invention, are chloride, bromide and iodide. Preferred polyhalide anions, according to the present invention, consist of chlorine, bromine and iodine atoms.

Onium cations, according to the present invention, may be polymeric or non-polymeric. Preferred non-polymeric onium salts for partial conversion of particles of substantially light-insensitive silver salt of an organic carboxylic acid into photo-sensitive silver halides according to the present invention are:

- PC01 = 3-(triphenyl-phosphonium)propionic acid bromide  
perbromide
- PC02 = 3-(triphenyl-phosphonium)propionic acid bromide
- PC03 = 3-(triphenyl-phosphonium)propionic acid iodide

The onium salts are present in quantities of between 0.1 and 35mol % with respect to the quantity of substantially light-insensitive organic silver salt of organic, with quantities between 0.5 and 20mol% being preferred and with quantities between 1 and 12mol % being particularly preferred.

#### Organic reducing agent

Suitable organic reducing agents for the reduction of said substantially light-insensitive organic heavy metal salts are organic compounds containing at least one active hydrogen atom linked to O, N or C. Particularly suitable organic reducing agents for the reduction the substantially light-insensitive silver salt of an organic carboxylic acid are non-sulfo-substituted 6-membered aromatic or heteroaromatic ring compounds with at least three substituents one of which is a hydroxy group at a first carbon atom and a second of which is a hydroxy or amino-group substituted on a

### Spectral sensitizer

According to a preferred embodiment of the present invention, the photo-addressable thermally developable element of the photothermographic recording material further comprises a dye with maximum absorbance in the wavelength range 600 to 1100nm.

The photo-addressable thermally developable element of the photothermographic recording material, according to the present invention, may contain a spectral sensitizer, optionally together with a supersensitizer, for the silver halide. The silver halide may be spectrally sensitized with various known dyes including cyanine, merocyanine, styryl, hemicyanine, oxonol, hemioxonol and xanthene dyes optionally, particularly in the case of sensitization to infra-red radiation, in the presence of a so-called supersensitizer. Useful cyanine dyes include those having a basic nucleus, such as a thiazoline nucleus, an oxazoline nucleus, a pyrroline nucleus, a pyridine nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus and an imidazole nucleus. Useful merocyanine dyes which are preferred include those having not only the above described basic nuclei but also acid nuclei, such as a thiohydantoin nucleus, a rhodanine nucleus, an oxazolidinedione nucleus, a thiazolidinedione nucleus, a barbituric acid nucleus, a thiazolinone nucleus, a malononitrile nucleus and a pyrazolone nucleus. In the above described cyanine and merocyanine dyes, those having imino groups or carboxyl groups are particularly effective. Suitable sensitizers of silver halide to infra-red radiation include those disclosed in the EP-A's 465 078, 559 101, 616 014 and 635 756, the JN's 03-080251, 03-163440, 05-019432, 05-072662 and 06-003763 and the US-P's 4,515,888, 4,639,414, 4,713,316, 5,258,282 and 5,441,866. Suitable supersensitizers for use with infra-red spectral sensitizers are disclosed in EP-A's 559 228 and 587 338 and in the US-P's 3,877,943 and 4,873,184.

### Thermal solvents

The above mentioned binders or mixtures thereof may be used in conjunction with waxes or "heat solvents" also called "thermal solvents" or "thermosolvents" improving the reaction speed of the redox-reaction at elevated temperature.

By the term "heat solvent" in this invention is meant a non-hydrolyzable organic material which is in a solid state in the

in which:

X represents O or N alkyl;  
each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> (same or different) represents hydrogen, alkyl, e.g. C1-C20 alkyl, preferably C1-C4 alkyl, cycloalkyl, e.g. cyclopentyl or cyclohexyl, alkoxy, preferably methoxy or ethoxy, alkylthio with preferably up to 2 carbon atoms, hydroxy, dialkylamino of which the alkyl groups have preferably up to 2 carbon atoms or halogen, preferably chlorine or bromine; or R<sup>1</sup> and R<sup>2</sup> or R<sup>1</sup> and R<sup>3</sup> represent the ring members required to complete a fused aromatic ring, preferably a benzene ring, or R<sup>3</sup> and R<sup>4</sup> represent the ring members required to complete a fused aromatic aromatic or cyclohexane ring.

A toner compound, according to the above general formula, particularly suited for use in combination with polyhydroxy benzene reducing agents is benzo[e][1,3]oxazine-2,4-dione.

#### Stabilizers and antifoggants

In order to obtain improved shelf-life and reduced fogging, stabilizers and antifoggants may be incorporated into the photothermographic materials of the present invention. Examples of suitable stabilizers and antifoggants and their precursors, which can be used alone or in combination, include the thiazolium salts described in US-P 2,131,038 and 2,694,716; the azaindenes described in US-P 2,886,437 and 2,444,605; the urazoles described in US-P 3,287,135; the sulfocatechols described in US-P 3,235,652; the oximes described in GB-P 623,448; the thiuronium salts described in US-P 3,220,839; the palladium, platinum and gold salts described in US-P 2,566,263 and 2,597,915; the tetrazolyl-thio-compounds described in US-P 3,700,457; the mesoionic 1,2,4-triazolium-3-thiolate stablizer precursors described in US-P 4,404,390 and 4,351,896; the tribromomethyl ketone compounds described in EP-A 600 587; the combination of isocyanate and halogenated compounds described in EP-A 600 586; the vinyl sulfone and  $\beta$ -halo sulfone compounds described in EP-A 600 589; and those compounds mentioned in this context in Chapter 9 of "Imaging Processes and Materials, Neblette's 8th edition", by D. Kloosterboer, edited by J. Sturge, V. Walworth and A. Shepp, page 279, Van Nostrand (1989); in Research Disclosure 17029 published in June 1978; and in the references cited in all these documents.

photothermographic recording material of the present invention. The anti-halation dye may also be bleached either thermally during the thermal development process, as disclosed in the US-P's 4,033,948, 4,088,497, 4,153,463, 4,196,002, 4,201,590, 4,271,263, 4,283,487, 4,308,379, 4,316,984, 4,336,323, 4,373,020, 4,548,896, 4,594,312, 4,977,070, 5,258,274, 5,314,795 and 5,312,721, or photo-bleached after removable after the thermal development process, as disclosed in the US-P's 3,984,248, 3,988,154, 3,988,156, 4,111,699 and 4,359,524. Furthermore the anti-halation layer may be contained in a layer which can be removed subsequent to the exposure process, as disclosed in US-P 4,477,562 and EP-A 491 457. Suitable anti-halation dyes for use with infra-red light are described in the EP-A's 377 961 and 652 473, the EP-B's 101 646 and 102 781 and the US-P's 4,581,325 and 5,380,635.

#### Support

The support for the photothermographic recording material according to the present invention may be transparent, translucent or opaque, e.g. having a white light reflecting aspect and is preferably a thin flexible carrier made e.g. from paper, polyethylene coated paper or transparent resin film, e.g. made of a cellulose ester, e.g. cellulose triacetate, corona and flame treated polypropylene, polystyrene, polymethacrylic acid ester, polycarbonate or polyester, e.g. polyethylene terephthalate or polyethylene naphthalate as disclosed in GB 1,293,676, GB 1,441,304 and GB 1,454,956. For example, a paper base substrate is present which may contain white reflecting pigments, optionally also applied in an interlayer between the recording material and the paper base substrate.

The support may be in sheet, ribbon or web form and subbed if needs be to improve the adherence to the thereon coated heat-sensitive recording layer.

Suitable subbing layers for improving the adherence of the thermosensitive element and the antistatic layer outermost backing layer of the present invention for polyethylene terephthalate supports are described e.g. in GB-P 1,234,755, US-P 3,397,988; 3,649,336; 4,123,278 and US-P 4,478,907 which relates to subbing layers applied from aqueous dispersion of sulfonated copolyesters, and further the subbing layers described in Research Disclosure published in Product Licensing Index, July 1967, p. 6.

A protective layer according to the present invention may comprise in addition at least one solid lubricant having a melting point below 150°C and at least one liquid lubricant in a binder, wherein at least one of the lubricants is a phosphoric acid derivative, further dissolved lubricating material and/or particulate material, e.g. talc particles, optionally protruding from the outermost layer. Examples of suitable lubricating materials are surface active agents, liquid lubricants, solid lubricants which do not melt during thermal development of the recording material, solid lubricants which melt (thermomeltable) during thermal development of the recording material or mixtures thereof. The lubricant may be applied with or without a polymeric binder. The surface active agents may be any agents known in the art such as carboxylates, sulfonates, aliphatic amine salts, aliphatic quaternary ammonium salts, polyoxyethylene alkyl ethers, polyethylene glycol organic carboxylic acid esters, fluoroalkyl C<sub>2</sub>-C<sub>20</sub> aliphatic acids. Examples of liquid lubricants include silicone oils, synthetic oils, saturated hydrocarbons and glycols. Examples of solid lubricants include various higher alcohols such as stearyl alcohol and organic carboxylic acids. Suitable slipping layer compositions are described in e.g. EP 138483, EP 227090, US-P 4,567,113, 4,572,860 and 4,717,711 and in EP-A 311841.

A suitable slipping layer being a layer comprising as binder a styrene-acrylonitrile copolymer or a styrene-acrylonitrile-butadiene copolymer or a mixture hereof and as lubricant in an amount of 0.1 to 10 % by weight of the binder (mixture) a polysiloxane-polyether copolymer or polytetrafluoroethylene or a mixture hereof.

Other suitable protective layer compositions that may be applied as slipping (anti-stick) coating are described e.g. in published European patent applications (EP-A) 0 501 072 and 0 492 411.

Such protective layers may also comprise particulate material, e.g. talc particles, optionally protruding from the protective outermost layer as described in WO 94/11198. Other additives can also be incorporated in the protective layer e.g. colloidal particles such as colloidal silica.

#### Antistatic layer

In a preferred embodiment the recording material of the present invention an antistatic layer is applied to the outermost layer on the side of the support not coated with the photo-addressable

e.g. has a blue colour.

In the hard copy field photothermographic recording materials on a white opaque base are used, whereas in the medical diagnostic field black-imaged transparencies are widely used in inspection techniques operating with a light box.

The following ingredients in addition to those mentioned above were used in the photothermographic recording materials of the examples and comparative examples illustrating this invention:

GELATIN 01: type K7598 from AGFA GELATINFABRIK vorm. KOEPPF & SOEHNE (a low viscosity gelatin)  
GELATIN 02: type K16353 from AGFA GELATINFABRIK vorm. KOEPPF & SOEHNE (a high viscosity gelatin)  
TMOS: tetramethylorthosilicate

The following examples and comparative examples illustrate the present invention. The percentages and ratios used in the examples are by weight unless otherwise indicated.

#### COMPARATIVE EXAMPLE 1

Extrapolation of the state of the art regarding photothermographic materials based on organic silver sulfinates disclosed in US-P 4,529,689 to photothermographic materials based on silver salts of organic carboxylic acids:

##### Silver heaxadecylsulfinat dispersion

5g of silver hexadecylsulfinat was mixed with 12.5mL of a 10% by weight aqueous solution of the non-ionic surfactant NON 03 and 82.5g of deionized water in a ball mill to produce a fine and stable dispersion of silver hexadecylsulfinat.

Partial conversion to photosensitive silver bromide and coating, drying and processing of the photothermographic material

EXPERIMENT A (= Invention example 13 in US-P 4,529,689):

The following ingredients were added with stirring to 6.8g of the silver hexadecylsulfinat dispersion: 1g of a 20% by weight

## Image-wise exposure and thermal processing

The photothermographic materials produced in experiments A, B, C and D of COMPARATIVE EXAMPLE 1 were then exposed to ultra-violet light through a test original in contact with the material in an Agfa-Gevaert™ DL 2000 exposure apparatus followed by heating on a heated metal block for 10s at 95°C to produce a very good image with a high contrast and good sharpness. The quality of the images obtained was assessed qualitatively and awarded a numerical score between 0 and 5 where these values correspond to:

- 0 = no image
- 1 = a very weak image
- 2 = a weak image
- 3 = a moderate image quality
- 4 = a good image
- 5 = a very good image with high contrast and good sharpness

The photothermographic materials from EXPERIMENTS A, B, C and D all exhibited a noticeably increased optical density after coating and drying. Image-wise exposure followed by thermal processing produced an increase in optical density, but without image discrimination for all the materials. All materials of EXPERIMENTS A, B, C and D were, therefore, all awarded a score of 0 for image quality.

The very poor imaging results obtained with the photothermographic materials of COMPARATIVE EXAMPLE 1 make the use of non-proteinaceous binders used in the invention examples of US-P 4,529,689 for other silver salt of an organic carboxylic acids such as the silver salts of organic carboxylic acids of the present invention not obvious to one skilled in the art.

## COMPARATIVE EXAMPLE 2

Extrapolation of the state of the art regarding photothermographic materials based on organic silver sulfonates disclosed in US-P 4,504,575 to photothermographic materials based on silver salts of organic carboxylic acids:



only with poor contrast. The materials of EXPERIMENTS A, B and C were, therefore, awarded score of 0, 0 and 1 respectively for image quality.

The very poor imaging results obtained with the photothermographic materials of COMPARATIVE EXAMPLE 2 make the use of non-proteinaceous binders such as the latex BINDER 57 used in the invention examples of US-P 4,504,575 for the coating of other silver salt of an organic carboxylic acids such as the silver salts of organic carboxylic acids of the present invention from aqueous media, not obvious to one skilled in the art.

#### COMPARATIVE EXAMPLES 3 to 5

In situ preparation of a silver behenate/silver halide-emulsion

Silver behenate was prepared by dissolving 34g (0.1 moles) of behenic acid in 340mL of 2-propanol at 65°C, converting the behenic acid to sodium behenate by adding 400mL of 0.25M aqueous sodium hydroxide to the stirred behenic acid solution and finally adding 250mL of 0.4M aqueous silver nitrate the silver behenate precipitating out. This was filtered off and then washed with a mixture of 10% by volume of 2-propanol and 90% by volume of deionized water to remove residual sodium nitrate.

After drying at 45°C for 12h, the silver behenate was dispersed in deionized water with the anionic dispersion agents Ultravon™ W and Mersolat™ H to produce after rapid mixing to a predispersion and homogenization with a microfluidizer a finely divided and stable dispersion containing 20% by weight of silver behenate, 2.1% by weight of Ultravon™ W and 0.203% by weight of Mersolat™ H. The pH of the resulting dispersion was adjusted to about 6.5.

Partial conversion to photosensitive silver halide and coating, drying and processing of the photothermographic material

For the material of comparative example 3, the following ingredients were then added to 1.5g of the silver behenate dispersion: 3g of a 10% by weight solution of GELATIN 01, 1g of a 2.2% by weight solution of PC01 [3-(triphenyl-phosphonium)propionic acid bromide] at a pH of 4 (i.e. ca. 8 mol% vs silver behenate) and 1g of a 4.5% by weight solution of 3-(3,4-dihydroxyphenyl)propionic

weight solution of GELATIN 01 was replaced by the binder and quantity of binder for the corresponding example in table 2. Table 2 also gives the % by weight of the binder in the dispersion medium in which the binder was added together with the pH of the binder dispersion.

Table 2:

Invent- ion example number	<u>Binder added to silver behenate emulsion</u>				Emul- sion layer addit- ive(s)	Image quality obtained after image-wise exposure and thermal processing
	<u>Binder numb- er(s)</u>	<u>solids wt% in medium in which binder is added</u>	<u>pH of binder disper- sion</u>	<u>quantity of binder added [g]</u>		
1	01	10	4.2	0.3	-	5
2	01	30	4.2	0.3	-	5
	29	2	4.2	0.012		
3	01	30	4.2	0.3	-	5
	29	2	4.2	0.03		
4	01	30	4.2	0.3	-	4
	60	10	4.2	0.1		
5	02	10	3.5	0.3	-	4
6	03	10	4.0	0.3	-	5
7	04	10	4.5	0.3	-	3
8	05	10	4.8	0.3	-	5
9	06	10	4.2	0.3	-	5
10	07	10	4.7	0.3	-	5
11	08	10	4.8	0.3	-	5
12	09	10	5.4	0.3	-	5
13	10	10	5.4	0.3	-	5
14	11	10	4.7	0.3	-	5
15	12	10	5.0	0.3	-	5
16	13	10	5.4	0.3	butylglycol- acetate	5
17	14	10	4.4	0.3	-	5
18	15	10	4.4	0.3	-	4
19	16	10	5.7	0.3	-	5
20	17	10	5.2	0.3	-	5
21	18	10	5.9	0.3	-	3
22	19	10	4.8	0.3	-	5

Table 2 (cont.):

Invent- ion example number	Binder added to silver behenate emulsion				Emul- sion layer addit- ive(s)	Image quality obtained after image-wise exposure and thermal processing
	Binder numb- er(s)	solids wt% in medium in which binder is added	pH of binder disper- sion	quantity of binder added [g]		
50	51	10	5.9	0.3	-	4
51	52	10	4.1	0.3	-	4
52	53	10	4.7	0.3	-	5
53	54	10	4.8	0.3	-	5
54	55	7.5		0.338	-	5
55	56	10	5.3	0.3	DOWANOL PM (9%)	4
56	57	10	4.6	0.3	-	4
57	58	10	7.5	0.3	-	4
58	59	10	7.4	0.3	-	3
59	60	5.5	6.1	0.3	-	5
60	60	5.5	6.1	0.3	-	5
	+ TMOS	24	2.0	0.24	-	5
61	61	5	7.7	0.3	-	3
62	62	5	4.5	0.3	-	4
63	63	5	5.8	0.3	-	3
64	64	5	6.5	0.3	-	3

The image quality results given in table 2 show that photothermographic silver behenate emulsion layers coated from aqueous media with water-soluble and water-dispersible polymers exhibit considerably improved image quality compared with those coated from aqueous media with gelatin as binder as taught by the state of the art.

Silver behenate photothermographic emulsion layers coated from aqueous media with styrene-containing, diene-containing and (meth)acrylate-containing copolymers as binders exhibit particularly good image qualities.

#### INVENTION EXAMPLE 65

A sodium behenate solution was prepared by first dissolving 34kg

dihydroxyphenylpropionic acid using a doctor blade coater with a slit-width of 50 $\mu$ m. After drying the resulting photothermographic material was image-wise exposed, thermally developed and the resulting image evaluated as described for COMPARATIVE EXAMPLE 1 except that the heating was carried out at 85°C for 30s instead of at 95°C for 10s. A good quality image was obtained with a low fog density meriting a numerical score of 4.

#### INVENTION EXAMPLE 66

The photothermographic recording material of invention example 66 was produced as described for invention example 65 except that the 1mL of a 30% by weight aqueous dispersion of BINDER 02 was replaced by 1mL of a 25% by weight aqueous dispersion of BINDER 22.

After drying the resulting photothermographic recording material was image-wise exposed, thermally developed and the image evaluated as described for INVENTION EXAMPLE 65. Similar photographic results were obtained to the photothermographic recording material of INVENTION EXAMPLE 65.

#### INVENTION EXAMPLE 67

The photothermographic recording material of invention example 65 was produced as described for invention example 63 except that the 1mL of a 30% by weight aqueous dispersion of BINDER 02 was replaced by 1mL of a 20% by weight aqueous dispersion of a BINDER 23.

After drying the resulting photothermographic recording material was image-wise exposed, thermally developed and the image evaluated as described for INVENTION EXAMPLE 65. Similar photographic results were obtained to the photothermographic material of INVENTION EXAMPLE 65.

#### INVENTION EXAMPLE 68

The photothermographic recording material of invention example 68 was produced as described for invention example 65 except that the 1mL of a 30% by weight aqueous dispersion of a terpolymer consisting of BINDER 02 was replaced by 1mL of BINDER 53.

After drying the resulting photothermographic recording material was image-wise exposed, thermally developed and the image evaluated

between these particles are silver bromide particles.

#### Coating and drying of the photothermographic material

A subbed polyethylene terephthalate support having a thickness of 100µm was doctor blade-coated with the silver behenate/silver bromide dispersion at a blade setting of 60µm. After drying for several minutes at 40°C on the coating bed, the emulsion layer was then doctor blade-coated with a 2.44% by weight aqueous solution of 3-(3,4-dihydroxyphenyl)propionic acid at a blade setting of 30µm. The resulting thermographic material was first allowed to dry on the coating bed for several minutes at 40°C and then was dried for 1 hour in a hot air oven at 50°C.

#### Image-wise exposure and thermal processing

The resulting photothermographic recording material was then image-wise exposed, thermally developed and the image evaluated as described for COMPARATIVE EXAMPLE 1. A very good image with a high contrast and good sharpness was obtained which was awarded a score of 5.

#### INVENTION EXAMPLE 70

The material of invention example 70 was prepared as described for invention example 69 except that the binder used was changed, 1g of a 30% by weight concentration of BINDER 02 being used instead of a 30% by weight concentration of BINDER 01. Image-wise exposure and thermal processing of the resulting material, as described for COMPARATIVE EXAMPLE 1, produced a very good image with a high contrast which was awarded a score of 5 for image quality as in the case of the material of invention example 69.

#### INVENTION EXAMPLE 71

The material of invention example 71 was prepared as described for invention example 69 except that the binder used was changed, 1g of a 30% by weight concentration of BINDER 03 being used instead of a 30% by weight concentration of BINDER 01. Image-wise exposure and thermal processing of the resulting material, as described for COMPARATIVE EXAMPLE 1, produced a very good image with a high

FIGURE:

FIGURE 1: shows a transmission electron micrograph at a magnification of 50,000x of the silver behenate/silver bromide dispersion produced in the course of the preparation of invention example 69.

7. Photothermographic recording material according to any of the preceding claims, wherein said photo-addressable thermally developable element further comprises a dye with maximum absorbance in the wavelength range 500 to 1100nm.
8. A process for producing a photothermographic recording material, according to any of claims 1 to 7, comprising the steps of: (i) producing a suspension of particles of a substantially light-insensitive silver salt of an organic carboxylic acid; (ii) producing an aqueous dispersion or aqueous dispersions containing ingredients necessary for photothermographic image formation; (iii) coating said aqueous dispersion or aqueous dispersions onto a support.
9. A process according to claim 8, wherein said suspension of particles of a substantially light-insensitive silver salt of an organic carboxylic acid is produced by simultaneous metered addition of an aqueous solution or suspension of an organic carboxylic acid, or its salt, and an aqueous solution of a silver salt to an aqueous liquid and said metered addition of said aqueous solution or suspension of said organic carboxylic acid or its salt; and/or said aqueous solution of said silver salt is regulated by the concentration of silver ions or the concentration of anions of said silver salt in said aqueous liquid.
10. A process for producing a photothermographic recording material according to claim 8 or 9, wherein said process further comprises the step of producing particles of said photosensitive silver halide from excess silver ions associated with particles of said substantially light-insensitive silver salt of an organic carboxylic acid.
11. A photothermographic recording process comprising the steps of: (i) image-wise exposing a photothermographic recording material, according to any of claims 1 to 7, to a source of actinic radiation to which said photothermographic recording material is sensitive; and (ii) thermally developing said image-wise exposed photothermographic recording material.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 96/02581

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 G03C1/498

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 386 761 A (FUJI PHOTO FILM CO., LTD.) 12 September 1990 see page 4, line 26 - line 30; claims; example 2	1,8,10, 11
Y	see page 40; example 5 ---	9
X	GB 1 362 970 A (EASTMAN KODAK COMPANY) 14 August 1974 see claims; example 3 ---	1,7,8, 10,11
X	EP 0 212 534 A (AGFA-GEVAERT AG) 4 March 1987 see page 4, line 33 - page 5, line 17; claims; examples see page 18, line 27 - page 19, line 22 ---	1-3,7,8, 10,11
Y	---	9
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Buscha, A



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Information on patent family members

International Application No

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